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# Preparation of Michael Adducts of Isobutyraldehyde and Acetylenecarboxylic Esters *via* *N*-Isobutylidene-*t*-butylamine

Shingo MIYAJIMA* and Kunio ITO

*Department of Applied Chemistry, Faculty of Engineering, Toyo University, Kawagoe, Saitama 350*

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*N*-Isobutylidene-*t*-butylamine reacted with methyl propiolate or dimethyl acetylenedicarboxylate to afford the Michael adducts predominantly. The adducts were converted to the corresponding formyl esters.

No Michael addition of isobutyraldehyde to acetylenecarboxylic esters has been reported, presumably because both the aldehyde and the acetylenes[1] undergo self-condensation in the presence of a strong base catalyst. The enamines derived from isobutyraldehyde react with electrophilic olefins to give 1,2- or 1,4-cycloaddition products,[2] which on hydrolytic ring opening yield Michael adducts. With acetylenecarboxylic esters, spontaneous rearrangement of initially formed cyclobutenes takes place and leads to dienamino esters.[3] Schiff's bases of $\alpha,\alpha$-disubstituted acetaldehydes are excellent complementary reagents to the enamines for the Michael addition to electrophilic olefins.[2a,4] With acetylenecarboxylic esters, however, only the formation of compounds resulting from *N*-alkenylation has been reported;[5] *N*-isobutylidenemethylamine, for example, reacts with two equivalents of dimethyl acetylenedicarboxylate to give a dihydropyridine derivative, a product of the reaction classified by Huisgen and Herbig[6] as a 1,4-dipolar cycloaddition.

We have investigated the reaction of *N*-isobutylidene-*t*-butylamine (**1**) with methyl propiolate (**2a**) or dimethyl acetylenedicarboxylate (**2b**) and found that the *t*-butyl group effectively prevents *N*-alkenylation, allowing the Michael addition to take place predominantly.

A solution of **2a** in tetrahydrofuran (THF) was gradually added to a stirred solution of **1** in THF heated at a bath temperature of 80 °C, and the heating was continued for an additional period of time. Fractional distillation afforded three isomeric products, the Michael adducts **3a** and **4a** and the enamino ester **5a**, in 45, 17, and 12% yields,

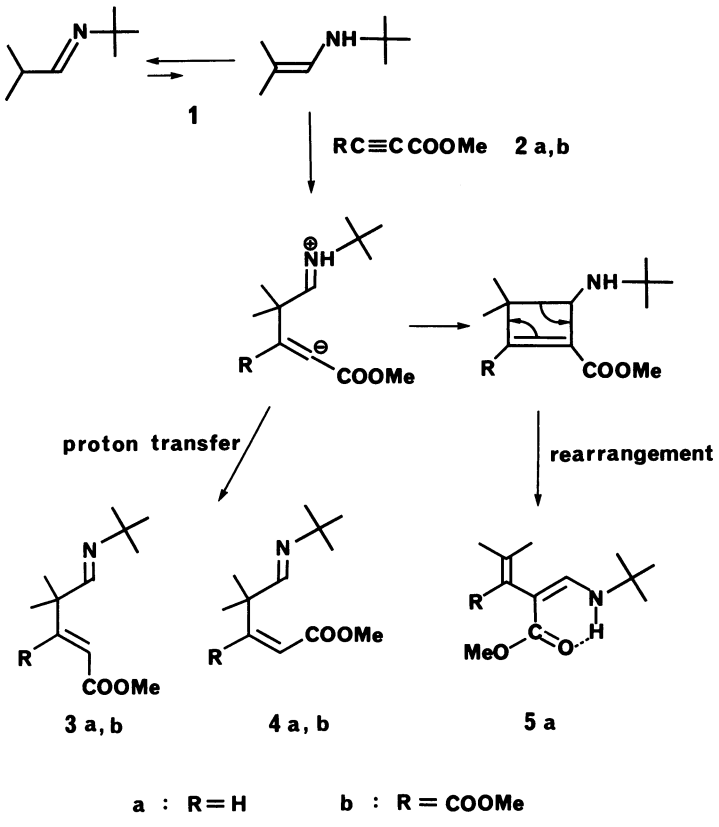


Fig. 1.

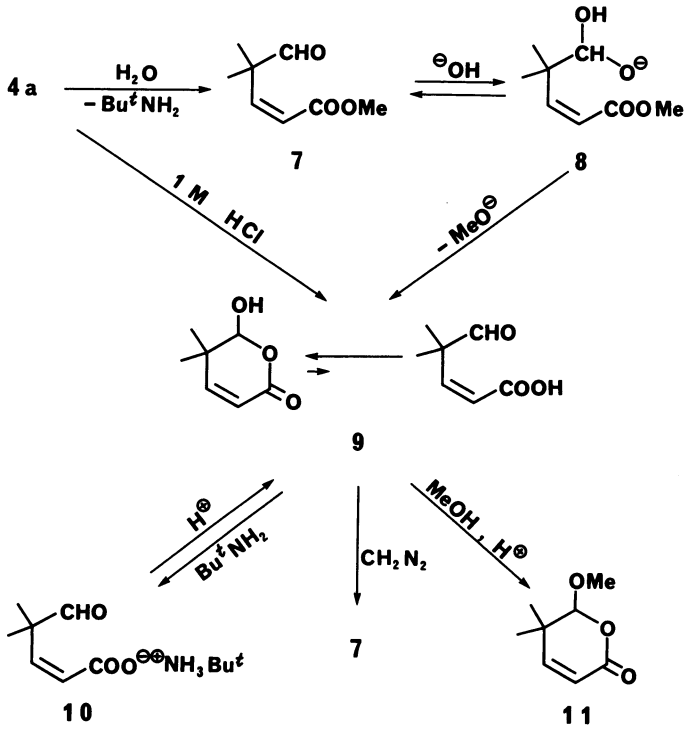
4a
$H_2O$
$-Bu^tNH_2$
CHO
COOMe
7
$^{\ominus}OH$
OH
CH
$O^{\ominus}$
COOMe
8
1 M HCl
$-MeO^{\ominus}$
OH
O
O
CHO
COOH
9
$H^{\oplus}$
$Bu^tNH_2$
$CH_2N_2$
$MeOH, H^{\oplus}$
CHO
$COO^{\ominus\oplus}NH_3Bu^t$
10
7
OMe
O
O
11

Fig. 2.

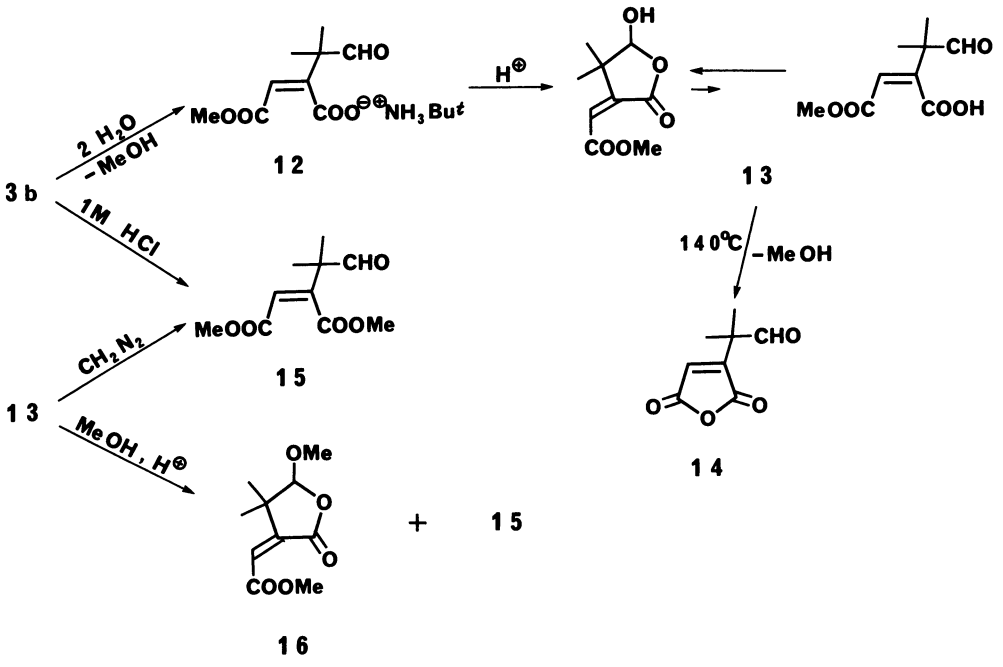
3b
$2\ H_2O$
$-MeOH$
CHO
MeOOC
$COO^{\ominus\oplus}NH_3Bu^t$
12
$H^{\oplus}$
OH
O
O
COOMe
13
CHO
MeOOC
COOH
1M HCl
CHO
MeOOC
COOMe
15
$CH_2N_2$
13
$MeOH, H^{\oplus}$
OMe
O
O
COOMe
16
+ 15
140°C
$-MeOH$
CHO
O
O
O
14

Fig. 3.

respectively (Fig. 1). These isomers were identified by their IR and $^1$H NMR spectra and elemental analyses.

Reaction of **1** with **2b** was carried out in a similar manner. Distillation gave a mixture of the Michael adducts **3b** and **4b**, as judged by its $^1$H NMR spectrum. When the mixture was heated at 160 °C for 2 h, isomerization took place and **3b** was obtained in 82% overall yield after distillation. The configuration of **3b** was further ascertained by its conversion to the maleic anhydride derivative **14**.

Apparently, the tautomeric enamine in equilibrium with the Schiff's base acts as a reacting species,[7] although the imino form is the only detectable form. The presumed pathways leading to the products are shown in Fig. 1.

The (*E*)-Michael adduct **3a**, on treatment with 1 M (1 M=1 mol dm$^{-3}$) HCl at room temperature, gave methyl (*E*)-4,4-dimethyl-5-oxo-2-pentenoate (**6**) in 94% yield.

The (*Z*)-adduct **4a**, on the other hand, was much less reactive under similar reaction conditions and both the imino and ester groups were slowly hydrolyzed to form the hydroxy lactone **9** (Fig. 2). Interestingly, when **4a** was stirred with water (50 times the weight of **4a**) at room temperature for 20 min, it went into solution and gave the carboxylate **10**. This rapid hydrolysis of the ester group of **4a** under such mild conditions can be explained in terms of intramolecular participation of the anion of the *gem*-diol in hydrolysis of **8**. The resulting hydroxy lactone **9**, which is in tautomeric equilibrium with the chain form,[8] combines with the initially liberated *t*-butylamine to afford **10**. Compound **9** was regenerated by acidification (85% yield based on **4a**).

When **9** was allowed to react with diazomethane, the (*Z*)-formyl ester **7** was obtained in 86% yield. Treatment of **9** with methanol containing $H_2SO_4$, on the other hand, gave the thermodynamically stabler[9] methoxy lactone **11** in a yield of 68%.

Similarly to **4a**, **3b** on treatment with water afforded the carboxylate **12**, which on acidification gave the hydroxy lactone **13** in 90% yield (Fig. 3). The formyl diester **15** was obtained by hydrolysis of **3b** with 1 M HCl in 79% yield. Alternatively, treatment of **13** with diazomethane gave a 92% yield of **15**. With methanol containing $H_2SO_4$ **13** yielded the methoxy lactone **16** (64%) along with a small amount of **15** (6%).

## Experimental

Melting and boiling points are uncorrected. GLPC analyses were carried out with a Hitachi 163 instrument using an SE-30 or a PEG-20 M column. IR spectra were recorded on a Hitachi 285 or 260-50 spectrometer; absorptions are given in cm$^{-1}$ in what follows. $^1$H NMR data were obtained with a Hitachi R-24B spectrometer; chemical shifts are reported in $\delta$ relative to TMS or DSS and coupling constants ($J$) in Hz in what follows. Microanalyses were performed at the Microanalysis Laboratory, Department of Chemistry, Faculty of Science, the University of Tokyo. The Schiff's base **1** was prepared according to the procedure of Tiollais.[10] Compound **2a** was obtained by the method of Ingold[11] using commercial potassium hydrogen acetylenedicarboxylate as a starting material. **2b** of commercial grade was used without further purification. THF was dried with 4A Molecular Sieve.

*Reaction of 1 with 2a.* To a stirred solution of **1** (63.6 g, 0.500 mol) in THF (60 ml) heated at a bath temperature of 80 °C was added a solution of **2a** (46.2 g, 0.550 mol) in THF (50 ml) over a period of 1 h. Stirring and heating were continued for an additional 10 h. Removal of the solvent *in vacuo* and distillation of the residue gave an isomeric mixture of methyl (*E*)-(**3a**), methyl (*Z*)-5-(*t*-butylimino)-4,4-dimethyl-2-pentenoate (**4a**), and methyl 2-(*t*-butylaminomethylene)-4-methyl-3-pentenoate (**5a**) in a ratio of 61:23:16 (determined by GLPC): bp 56.0—92.0 °C/0.90 mmHg (1 mmHg=133.322 Pa); 87.9 g (83% based on **1**). Each isomer was isolated by redistillation through a 50 cm spinning band column; 47.5 g (45%) of **3a**, 18.0 g (17%) of **4a**, and 12.6 g (12%) of **5a** were obtained.

**3a**: bp 70.0—72.0 °C/0.90 mmHg; IR (neat) 1724 (C=O), 1670 (C=N), 1645 (C=C), and 977 ($^{H}\!>\!C\!=\!C\!<^{H}$); $^1$H NMR ($CDCl_3$) 1.15 (s, 9H, $C(CH_3)_3$), 1.23 (s, 6H, $C(CH_3)_2$), 3.71 (s, 3H, $CO_2CH_3$), 5.76 (d, $J$=16, 1H, CH=C<u>H</u>$CO_2$Me), 7.00 (d, $J$=16, 1H, C<u>H</u>=CH$CO_2$Me), and 7.44 (s, 1H, CH=N). Found: C, 68.50; H, 10.18; N, 6.60%. Calcd for $C_{12}H_{21}NO_2$: C, 68.21; H, 10.02; N, 6.63%.

**4a**: bp 56.5—57.5 °C/0.90 mmHg; IR (neat) 1727 (C=O), 1663 (C=N), and 1637 (C=C); $^1$H NMR ($CDCl_3$) 1.12 (s, 9H, $C(CH_3)_3$), 1.31 (s, 6H, $C(CH_3)_2$), 3.62 (s, 3H, $CO_2CH_3$), 5.77 (d, $J$=12, 1H, CH=C<u>H</u>$CO_2$Me), 6.28 (d, $J$=12, 1H, C<u>H</u>=CH$CO_2$Me), and 7.63 (s, 1H, CH=N). Found: C, 68.44; H, 9.78; N, 6.68%. Calcd for $C_{12}H_{21}NO_2$: C, 68.21; H, 10.02; N, 6.63%.

**5a**: bp 87.0—90.0 °C/0.90 mmHg; IR (neat) 3285 (NH), 1665 (C=O), and 1604 (C=C); $^1$H NMR ($CDCl_3$) 1.28 (s, 9H, $C(CH_3)_3$), 1.68 (d, $J$=1.5, 3H, $C(CH_3)_2$), 1.76 (d, $J$=1.5, 3H, $C(CH_3)_2$), 3.63 (s, 3H, $CO_2CH_3$), 5.81 (m, 1H, C<u>H</u>=$C(CH_3)_2$), 6.76 (d, $J$=14, 1H, =C<u>H</u>NH), and 8.23 (br d, $J$=14, 1H, NH). Addition of $CD_3OD$ containing a trace of HCl resulted in loss of the signal at 8.23 and collapse of the signal at 6.76 to a singlet. Found: C, 68.04; H, 10.15; N, 6.56%. Calcd for $C_{12}H_{21}NO_2$: C, 68.21; H, 10.02; N, 6.63%.

*Reaction of 1 with 2b.* To a stirred solution of **1** (127.2 g, 1.00 mol) in THF (260 ml) heated at a bath temperature of 70 °C was added a solution of **2b** (142.1 g, 1.00 mol) in THF (280 ml) during 1 h. Stirring and heating were continued for an additional 1 h. The solvent was removed *in vacuo* and the residue was distilled to give 222.7 g of the main fraction boiling at 107.0—111.0 °C (0.60 mmHg). GLPC on an SE-30 or a PEG-20 M column showed virtually a single peak. $^1$H NMR analysis, however, indicated a mixture of the geometrical isomers, dimethyl [2-(*t*-butylimino)-1,1-dimethylethyl]maleate (**3b**) and dimethyl [2-(*t*-butylimino)-1,1-dimethylethyl]fumarate

(**4b**), in a ratio of *ca.* 70:30; besides the signals due to **3b**, which will be shown below, those attributable to **4b** were observed: 1.11 (s, 9H, $C(CH_3)_3$), 1.40 (s, 6H, $C(CH_3)_2$), 3.73 (s, 3H, $CO_2CH_3$), 3.81 (s, 3H, $CO_2CH_3$), 6.49 (s, 1H, C=CH), and 7.58 (s, 1H, CH=N).

The mixture was heated at 160 °C for 2 h and distillation gave 219.7 g (82% based on **1**) of **3b**: bp 88.5—89.0 °C/0.15 mmHg; IR (neat) 1732 (C=O), 1655 (C=N), and 1639 (C=C); $^1$H NMR ($CDCl_3$) 1.16 (s, 9H, $C(CH_3)_3$), 1.30 (s, 6H, $C(CH_3)_2$), 3.73 (s, 3H, $CO_2CH_3$), 3.81 (s, 3H, $CO_2CH_3$), 5.86 (s, 1H, C=CH), and 7.51 (s, 1H, CH=N). Found: C, 62.34; H, 8.90; N, 5.05%. Calcd for $C_{14}H_{23}NO_4$: C, 62.43; H, 8.61; N, 5.20%.

*Methyl (E)-4,4-Dimethyl-5-oxo-2-pentenoate (6).* A mixture of **3a** (30.0 g, 0.142 mol) and 1 M HCl (220 ml) was stirred for 1 h at room temperature. The reaction mixture was extracted with ether (3×150 ml). The ethereal extract was washed with aq $NaHCO_3$, dried ($Na_2SO_4$), concentrated, and distilled, giving 20.9 g (94%) of **6**: bp 64.5—65.0 °C/0.75 mmHg; IR (neat) 1725 (C=O), 1650 (C=C), and 982 ($H>C=C<H$); $^1$H NMR ($CDCl_3$) 1.26 (s, 6H, $C(CH_3)_2$), 3.71 (s, 3H, $CO_2CH_3$), 5.88 (d, $J$=16, 1H, CH=C<u>H</u>$CO_2$Me), 6.91 (d, $J$=16, 1H, C<u>H</u>=CH$CO_2$Me), and 9.41 (s, 1H, CHO). Found: C, 61.46; H, 7.90%. Calcd for $C_8H_{12}O_3$: C, 61.52; H, 7.74%. 2,4-Dinitrophenylhydrazone, mp 124.0—124.4 °C (from methanol). Found: C, 50.18; H, 4.64; N, 16.83%. Calcd for $C_{14}H_{16}N_4O_6$: C, 50.00; H, 4.80; N, 16.66%.

*6-Hydroxy-5,5-dimethyl-5,6-dihydro-2H-pyran-2-one (9).* The (*Z*)-imino ester **4a** (12.7 g, 0.0601 mol) was stirred with water (640 ml) at room temperature. After 20 min, it went into solution. The solution was washed with ether (100 ml) and concentrated with a rotary evaporator below 55 °C *in vacuo* until some crystals began to separate out. To the residue, 4 M HCl (18 ml) was added, and the resulting solution was extracted with ether (3×50 ml). The ethereal extract was dried ($Na_2SO_4$) and evaporated, leaving 7.22 g (85%) of **9**[12] as a crystalline solid, mp 62.0—64.0 °C. A sample was recrystallized from ether–hexane for analysis: mp 65.0—65.8 °C; IR (KBr) 3270 (OH) and 1670 (C=O); $^1$H NMR ($CDCl_3$) 1.17 (s, 6H, $C(CH_3)_2$), 5.38 (d, $J$=1, 1H, CH), 5.81 (br s, 1H, OH, caused to disappear by adding $D_2O$), 5.88 (d, $J$=9.5, 1H, CH=C<u>H</u>CO), and 6.59 (dd, $J$=9.5, 1, 1H, C<u>H</u>=CHCO). (Found: C, 59.29; H, 7.38%)

*t-Butylammonium (Z)-4,4-Dimethyl-5-oxo-2-pentenoate (10).* A mixture of **4a** (18.5 mg) and $D_2O$ (0.93 ml) was shaken at room temperature for 20 min. The $^1$H NMR spectrum of the resulting solution was identical with that of **10** prepared as follows.

*t*-Butylamine (0.397 g, 5.43 mmol) was added dropwise to a solution of **9** (0.712 g, 5.01 mmol) in water (1.0 ml). The reaction mixture was cooled, and the precipitated crystals were collected and dried with KOH pellets *in vacuo* (0.785 g, 73%): mp 111.5—113.0 °C; IR (KBr) 3000—2800 ($\overset{+}{N}H_3$), 1726 (C=O), 1637 (C=C), 1540 ($\overset{+}{N}H_3$), and 1416 ($COO^-$); $^1$H NMR ($D_2O$) 1.20 (s, 6H, $C(CH_3)_2$), 1.34 (s, 9H, $C(CH_3)_3$), 5.82 (d, $J$=12, 1H, CH=C<u>H</u>$COO^-$), 5.85 (d, $J$=12, 1H, C<u>H</u>=CH$COO^-$), and 9.23 (s, 1H, CHO). Found: C, 61.51; H, 9.83; N, 6.49%. Calcd for $C_{11}H_{21}NO_3$: C, 61.37; H, 9.83; N, 6.51%.

*Acid-catalyzed Hydrolysis of 4a.* To 86.5 mg (0.409 mmol) of **4a** was added 0.60 ml of 1 M HCl in $D_2O$. The $^1$H NMR spectrum of the resulting iminium salt showed signals at 1.46 (s, 9H, $C(CH_3)_3$), 1.55 (s, 6H, $C(CH_3)_2$), 3.76 (s, 3H, $CO_2CH_3$), 6.12 (d, $J$=12, 1H, CH=C<u>H</u>$CO_2$Me), 6.57 (d, $J$=12, 1H, C<u>H</u>=CH$CO_2$Me), and 8.72 (s, 1H, CH=$\overset{+}{N}$). With the salt kept standing at room temperature for 1 d, the peak areas of the $CO_2CH_3$ protons and the CH=$\overset{+}{N}$ proton decreased to 25 and 24% of their initial areas, respectively, relative to the total area of the olefinic protons. After 2 d, the spectrum indicated the completion of reaction, *i.e.*, an approximately equimolar mixture of **9**, $CH_3OD$, and *t*-butylammonium chloride.

*Methyl (Z)-4,4-Dimethyl-5-oxo-2-pentenoate (7).* Diazomethane was fed into a stirred solution of **9** (5.80 g, 40.8 mmol) in ether (100 ml) with $N_2$ as a carrier gas until a yellow color persisted for several min. An air condenser was attached and the solution was refluxed to remove the excess of diazomethane. Evaporation and distillation gave 5.45 g (86%) of **7**:[12] bp 49.0—49.3 °C/0.80 mmHg; IR (neat) 1722 (C=O) and 1637 (C=C); $^1$H NMR ($CDCl_3$) 1.30 (s, 6H, $C(CH_3)_2$), 3.67 (s, 3H, $CO_2CH_3$), 5.93 (d, $J$=12, 1H, CH=C<u>H</u>$CO_2$Me), 6.18 (d, $J$=12, 1H, C<u>H</u>=CH$CO_2$Me), and 9.46 (s, 1H, CHO). (Found: C, 61.32; H, 7.97%) 2,4-Dinitrophenylhydrazone, mp 119.8—120.2 °C (from methanol). Found: C, 50.16; H, 4.65; N, 16.53%. Calcd for $C_{14}H_{16}N_4O_6$: C, 50.00; H, 4.80; N, 16.66%.

*6-Methoxy-5,5-dimethyl-5,6-dihydro-2H-pyran-2-one (11).* A solution of **9** (2.00 g, 14.1 mmol) in methanol (40 ml) containing concd $H_2SO_4$ (0.078 g) was allowed to stand at room temperature for 3 h. The solution was poured into satd aq NaCl (120 ml) and the mixture was extracted with ether (3×60 ml). The ethereal extract was dried ($Na_2SO_4$), concentrated, and distilled to afford 1.49 g (68%) of **11**: bp 71.0—72.0 °C/1.0 mmHg; IR (neat) 1723 (C=O); $^1$H NMR ($CDCl_3$) 1.11 (s, 3H, $CCH_3$), 1.18 (s, 3H, $CCH_3$), 3.54 (s, 3H, $CO_2CH_3$), 4.85 (d, $J$=1, 1H, CH), 5.86 (d, $J$=9.5, 1H, CH=C<u>H</u>CO), and 6.53 (dd, $J$=9.5, 1, 1H, C<u>H</u>=CHCO). Found: C, 61.28; H, 7.88%. Calcd for $C_8H_{12}O_3$: C, 61.52; H, 7.74%.

*Methyl (Z)-5-Hydroxy-4,4-dimethyl-2-oxotetrahydrofuran-$\Delta^{3,\alpha}$-acetate (13).* A mixture of **3b** (80.8 g, 0.300 mol) and water (4000 ml) was stirred at room temperature for 2.5 h. The resulting solution was washed with ether (2×400 ml) and concentrated on a rotary evaporator below 55 °C *in vacuo* until some crystals began to separate out. To the residue was added 80 ml of 4 M HCl, and the resulting solution was extracted with ether (3×150 ml). The ethereal extract was dried ($Na_2SO_4$) and evaporated, leaving 54.3 g (90%) of **13** as a crystalline solid; mp 71.0—75.0 °C. A sample was recrystallized from ether–hexane for analysis: mp 77.1—77.5 °C; IR (KBr) 3295 (OH), 1775, 1710 (C=O), and 1670 (C=C); $^1$H NMR ($CDCl_3$) 1.25 (s, 6H, $C(CH_3)_2$), 3.82 (s, 3H, $CO_2CH_3$), 5.60 (s, 1H, CH), 5.72 (br s, 1H, OH, caused to disappear by adding $D_2O$), and 6.25 (s, 1H, C=CH). Found: C, 54.24; H, 6.26%. Calcd for $C_9H_{12}O_5$: C, 54.00; H, 6.04%.

*t-Butylammonium (Z)-2-(1,1-Dimethyl-2-oxoethyl)-3-methoxycarbonylacrylate (12).* A mixture of **3b** (28.0 mg) and $D_2O$ (1.40 ml) was stirred at room temperature for 2.5 h. The $^1$H NMR spectrum of the resulting solution was identical with that of **12** prepared as follows.

To a suspension of **13** (0.807 g, 4.03 mmol) in water (1.0 ml) warmed to 50 °C was added *t*-butylamine (0.298 g,

4.07 mmol). The resulting solution was cooled, and the precipitated crystals were collected and dried with KOH pellets *in vacuo* (0.548 g, 50%): mp 113.5—114.5 °C; IR (KBr) 3000—2800 ($\overset{+}{N}H_3$), 1720 (C=O), 1634 (C=C), 1540 ($\overset{+}{N}H_3$), and 1400 ($COO^-$); $^1$H NMR ($D_2O$) 1.25 (s, 6H, $C(CH_3)_2$), 1.36 (s, 9H, $C(CH_3)_3$), 3.70 (s, 3H, $CO_2CH_3$), 5.69 (s, 1H, C=CH), and 9.33 (s, 1H, CHO). Found: C, 57.29; H, 8.77; N, 5.07%. Calcd for $C_{13}H_{23}NO_5$: C, 57.13; H, 8.48; N, 5.12%.

*(1,1-Dimethyl-2-oxoethyl)maleic Anhydride (14).* Compound **13** (40.0 g, 0.200 mol) was heated at 140 °C for 2 h under reduced pressure (20 mmHg). Distillation afforded 32.7 g (97%) of **14**: bp 103.0—106.0 °C/0.25 mmHg; mp 31.0—31.9 °C; IR (KBr) 1835, 1766, 1716 (C=O), and 1628 (C=C); $^1$H NMR ($CDCl_3$) 1.51 (s, 6H, $C(CH_3)_2$), 6.76 (s, 1H, C=CH), and 9.50 (s, 1H, CHO). Found: C, 57.21; H, 4.78%. Calcd for $C_8H_8O_4$: C, 57.14; H, 4.80%.

*Dimethyl (1,1-Dimethyl-2-oxoethyl)maleate (15).*

*Acidcatalyzed Hydrolysis of 3b*: A mixture of **3b** (40.0 g, 0.149 mol) and 1 M HCl (300 ml) was stirred at room temperature for 10 min. Ether (200 ml) was added and stirring was continued for an additional 2 h. The ether layer was separated and the aq layer was extracted with ether (3×150 ml). The combined extracts were washed with a small amount of water, dried ($Na_2SO_4$), concentrated, and distilled, giving 25.0 g (79%) of **15**: bp 100.0—101.0 °C/0.50 mmHg; IR (neat) 1735, 1725 (C=O), and 1641 (C=C); $^1$H NMR ($CDCl_3$) 1.28 (s, 6H, $C(CH_3)_2$), 3.70 (s, 3H, $CO_2CH_3$), 3.79 (s, 3H, $CO_2CH_3$), 5.91 (s, 1H, C=CH), and 9.38 (s, 1H, CHO). Found: C, 56.08; H, 6.88%. Calcd for $C_{10}H_{14}O_5$: C, 56.07; H, 6.59%. 2,4-Dinitrophenylhydrazone, mp 145.9—146.1 °C (from methanol). Found: C, 48.71; H, 4.47; N, 14.31%. Calcd for $C_{16}H_{18}N_4O_8$: C, 48.73; H, 4.60; N, 14.21%.

*Formyl Diester 15 from 13*: Treatment of **13** (16.0 g, 79.9 mmol) in ether (200 ml) with diazomethane and working up in the same manner as employed in the preparation of **7** yielded 15.8 g (92%) of a material boiling at 102.0—103.5 °C (0.65 mmHg), whose IR and $^1$H NMR spectra were identical with those of **15** prepared as described above.

*Methyl (Z)-5-Methoxy-4,4-dimethyl-2-oxotetrahydrofuran-$\Delta^{3,\alpha}$-acetate (16).* A solution of **13** (3.01 g, 15.0 mmol) in methanol (60 ml) containing concd $H_2SO_4$ (0.11 g) was allowed to stand at room temperature for 4 h. The solution was poured into 180 ml of satd aq NaCl and the mixture was extracted with ether (2×90 ml). The ethereal extract was dried ($Na_2SO_4$), concentrated, and distilled with a 15 cm concentric column, giving 0.20 g (6%) of **15** (bp 99.0—101.5 °C/0.50 mmHg) and 2.05 g (64%) of **16** (bp 109.0—110.0 °C/0.50 mmHg, mp 68.0—69.6 °C). A sample of **16** was recrystallized from hexane–$CCl_4$ for analysis: mp 70.6—71.3 °C; IR (KBr) 1761, 1728 (C=O), and 1672 (C=C); $^1$H NMR ($CCl_4$) 1.19 (s, 3H, $CCH_3$), 1.22 (s, 3H, $CCH_3$), 3.48 (s, 3H, $OCH_3$), 3.73 (s, 3H, $CO_2CH_3$), 4.95 (s, 1H, CH), and 6.08 (s, 1H, C=CH). Found: C, 56.02; H, 6.68%. Calcd for $C_{10}H_{14}O_5$: C, 56.07; H, 6.59%.

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